Hirshfeld atoms in molecules revisited

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The well-known Hirshfeld [1] method for the atom in the molecule has been criticized by several authors [2-6] as being a quite arbitrary method to describe the atom in the molecule (AIM). Bultinck et al. [5-6] recently described a self-consistent Hirshfeld scheme where this arbitrariness was removed by letting the molecule decide its own promolecule. The weight function for the AIM A is given by:

$$w_A\left(\mathbf{r}, N_A^0\right) = \frac{\rho_A^0\left(\mathbf{r}, N_A^0\right)}{\sum_A \rho_A^0\left(\mathbf{r}, N_A^0\right)}$$

Where explicitly the dependence on the number of electrons N_A in AIM A is indicated. The AIM density $\rho_A(\mathbf{r})$ is then obtained by letting the weight act on the molecular density $\rho(\mathbf{r})$:

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho(\mathbf{r}) \quad \wedge \qquad N_A = \int \rho_A(\mathbf{r})\, d\mathbf{r}$$

The key feature of the Hirshfeld-I method is that the Hirshfeld process is repeated until $N_A^0 = N_A$. In this presentation the information theoretic context of Hirshfeld-I is sketched, performance of the method compared to regular Hirshfeld analysis discussed [5-7], its impact on the nature of atom condensed Fukui functions described [8] and its use for good quality monopole approximation electrostatic potentials shown [9].

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